



PRIORITY DOCUMENT

SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

The Patent Office
Concept House
Cardiff Road
Newport
South Wales
NP10 8QQ

REC'D 04 DEC 2003

WIPO PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

I also certify that the attached copy of the request for grant of a Patent (Form 1/77) bears an amendment, effected by this office, following a request by the applicant and agreed to by the Comptroller-General.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.

Signed *Andrew George*
Dated 13 November 2003

Patents Form 1/77

R. Act 1977
(Rule 16)The
Patent
Office

THE PATENT

A

30 OCT 2002

RECEIVED BY FAX

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form.)

30 OCT 2002 E759998-1 010101
P01/7700'0.50-0225177.5

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RR

1. Your reference

500067/GB

TC-MP100272-WO

2. Patent application number

(The Patent Office will fill in this part)

0225177.5

30 OCT 2002

3. Full name, address and postcode of the or of each applicant (including all surnames)

INEOS Silicas Limited
Bank Quay
Warrington
Cheshire WA5 1AB
United Kingdom

Patents ADP number (if you know it)

8465379001

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

STABILISED ALUMINOSILICATE SLURRIES

5. Name of your agent (if you have one)

John Derek JACKSON

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

INEOS Silicas Limited
Bank Quay
Warrington
Cheshire WA5 1AB
United Kingdom

Liam Wren McNeight

Highbank House Lawrence

Exchange Street Stockport Cheshire

SK3 0ET

8465379001

Patents ADP number (if you know it)

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country

Priority application number
(if you know it)Date of filing
(day / month / year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application

Date of filing
(day / month / year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request? (Answer 'Yes' if:

YES

- any applicant named in part 3 is not an inventor, or
- there is an inventor who is not named as an applicant, or
- any named applicant is a corporate body.

See note (d))

9. Enter the number of sheets for any of the following items you are filing with this form.
Do not count copies of the same document

Continuation sheets of this form

Description	8
Claim(s)	2
Abstract	1

Drawing(s)

10. If you are also filing any of the following, state how many against each item.

Priority documents

Translations of priority documents

Statement of inventorship and right to grant of a patent (Patents Form 7/77)

Request for preliminary examination and search (Patents Form 9/77)

Request for substantive examination (Patents Form 10/77)

Any other documents
(please specify)

11.

I/We request the grant of a patent on the basis of this application.

Signature

John Derek JACKSON

Date

30 Oct. 2002

12. Name and daytime telephone number of person to contact in the United Kingdom

John Derek JACKSON

01925 416120

Warning

After an application for a patent has been filed, the Comptroller of the Patent Office will consider whether publication or communication of the invention should be prohibited or restricted under Section 22 of the Patents Act 1977. You will be informed if it is necessary to prohibit or restrict your invention in this way. Furthermore, if you live in the United Kingdom, Section 23 of the Patents Act 1977 stops you from applying for a patent abroad without first getting written permission from the Patent Office unless an application has been filed at least 6 weeks beforehand in the United Kingdom for a patent for the same invention and either no direction prohibiting publication or communication has been given, or any such direction has been revoked.

Notes

- If you need help to fill in this form or you have any questions, please contact the Patent Office on 0645 500505.
- Write your answers in capital letters using black ink or you may type them.
- If there is not enough space for all the relevant details on any part of this form, please continue on a separate sheet of paper and write "see continuation sheet" in the relevant part(s). Any continuation sheet should be attached to this form.
- If you have answered 'Yes' Patents Form 7/77 will need to be filed.
- Once you have filled in the form you must remember to sign and date it.
- For details of the fee and ways to pay please contact the Patent Office.

STABILISED ALUMINOSILICATE SLURRIES

This invention relates to aqueous slurries of crystalline aluminosilicates and in particular to crystalline aluminosilicate slurries having controlled rheological properties.

5

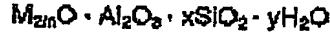
Crystalline aluminosilicates, or zeolites, have found use as fillers in such applications as the manufacture of paper. For such use, it is convenient to transport the zeolite in bulk in the form of an aqueous slurry. Particularly useful aqueous zeolite slurries having a relatively low pH value and containing a multivalent salt in addition to the zeolite are described in PCT application published as WO 01/94512. These slurries are stable and do not settle on standing but, because they have a lightly gelled structure, they can sometimes be difficult to fully discharge from a vessel.

10 An object of this invention is to provide a modified version of such a slurry having a structure which is resistant to settling but is readily capable of being discharged from a vessel.

15 According to the invention, an aqueous slurry comprises

(a) a crystalline aluminosilicate represented by the empirical formula

20



wherein M represents a first metal moiety, said first metal having a valency of n, x indicates the ratio of atoms of silicon to atoms of aluminium and y indicates the ratio of molecules of water to atoms of aluminium,

25

(b) a salt of a second metal selected from the group consisting of Group III metals, metallic elements of Group IV, magnesium, titanium, chromium, iron, nickel, copper, zinc, zirconium and silver, said salt of a second metal being present in an amount which is sufficient to replace from about 2.0 to about 40 per cent by weight of the first metal moiety, and

30

(c) particulate silica having a BET surface area greater than 500 m²/g and a pore volume, as measured by nitrogen manometry of less than 2.1 cm³/g.

The above form of empirical formula is used for simplicity in expressing the molar ratios of the components, but it can be seen that the ratio of Si atoms to Al atoms in this formula is equal to x/2 and the ratio of water molecules to Al atoms is equal to y/2.

35

The first metal M can be any metal capable of forming a crystalline aluminosilicate structure having the above empirical formula. Preferably, M is an alkali metal and the preferred alkali metal is sodium.

60006

2

The crystalline aluminosilicates used in the invention are usually known as zeolites and can have the structure of any of the known zeolites. The structure and characteristics of many zeolites are described in the standard work "Zeolite Molecular Sieves" by Donald W. Breck, published by Robert E. Krieger Publishing Company. Usually, the value of x in the above empirical formula is in the range 1.6 to 10. The value of y, which represents the amount of water contained in the voids of the zeolite, can vary widely. In anhydrous material y = 0 and, in fully hydrated zeolites, y is typically up to 5.

Zeolites useful in this invention may be based on naturally-occurring or synthetic aluminosilicates and the preferred forms of zeolite have the structure known as zeolite P, zeolite X or zeolite A. Particularly preferred forms of zeolite are those disclosed in EP-A-0 384 070, EP-A-0 885 364, EP-A-0 697 010, EP-A-0 742 780, WO-A-96/14270, WO-A-96/34828 and WO-A-97/06102, the entire contents of which are incorporated herein by this reference. The zeolite P described in EP-A-0 384 070 has the empirical formula given above in which M represents an alkali metal and x has a value up to 2.66, preferably in the range 1.8 to 2.66, and has a structure which is particularly useful in the present invention.

The preferred amount of the salt of a second metal used to prepare mixtures used in the invention depends upon a number of factors, such as the actual second metal selected, the actual crystalline aluminosilicate chosen and the desired effect to be achieved (in particular, the desired pH of the slurry). Useful mixtures contain an amount of second metal salt sufficient to replace from 3.0 to 30 per cent by weight of first metal, and, more preferably, from 3.0 to 20 per cent by weight of the first metal.

The appropriate amount of salt of a second metal in the mixture used in the invention, expressed in grams, depends upon the composition of the zeolite and the charge on the second metal but is readily calculated by a skilled person. For example, a zeolite having the empirical formula

30 $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$
(anhydrous type A zeolite) contains 16.2 g of Na per 100 g of zeolite. An aluminium ion is capable of replacing three sodium ions. Hence, making allowance for the atomic weights of sodium and aluminium, it can be calculated that a mixture containing 100 g of anhydrous zeolite A and 0.317 g Al in the form of a suitable salt is a mixture suitable for use in the invention and containing sufficient salt of a second metal (i.e. aluminium) to replace 5 per cent by weight of the first metal moiety (i.e. sodium).

50008

It has been observed that a salt of a second metal wherein the ion of the second metal has a relatively small size or a relatively high charge is more effective as a means of controlling the pH of the zeolite slurry. Consequently, the effect of the metal salt on the pH of the slurry is more marked when the salt of a second metal is a salt of aluminium than when it is a salt of magnesium and the effect is more marked for salts of magnesium than for salts of zinc. The preferred second metals for use in the invention are aluminium, zirconium and tin.

Slurries useful in the paper industry preferably have an approximately neutral pH. 10 Particularly useful slurries of this invention contain an amount of the second metal which is sufficient to produce a slurry having a pH in the range 8 to 9, preferably in the range 7 to 9.

15 The particle size of the crystalline aluminosilicates used in the slurries of this invention is adjusted to suit the intended use. Typically, the volume average particle size will be greater than 0.1 μm and, usually, less than 20 μm . More preferably, the crystalline aluminosilicates will have a volume average particle size in the range 0.5 to 10 μm . For use as a filler for papers, the crystalline aluminosilicate preferably has a volume average particle size in the range 1 to 5 μm .

20 Various methods of assessing particle size are known and all give slightly different results. In the present invention, a size distribution is obtained by light scattering from particles dispersed by ultrasound in demineralised water using a Malvern Mastersizer®. The volume average particle size is the average particle size at 50 per cent cumulative volume as determined from the distribution.

30 The amount of crystalline aluminosilicate, expressed as dry weight of aluminosilicate present in the slurry is usually above 20 per cent by weight and often above 30 per cent by weight. The upper practical limit on the amount of aluminosilicate in the slurry will depend upon the viscosity of the slurry, which is likely to be too high for use in many applications when more than 65 per cent dry weight of aluminosilicate is present. Generally, useful slurries consisting essentially of crystalline aluminosilicate, salt of a second metal, silica and water, according to this invention, will contain not more than 50 per cent by weight of aluminosilicate (on a dry basis). For the purposes of this invention dry aluminosilicate is considered to be aluminosilicate which has been heated at 105° C to constant weight.

60008

4

The slurry of the invention contains a salt of a second metal as hereinbefore specified. Mixtures of more than one salt of a second metal (as defined) or salts of more than one second metal (as defined) can be used. Suitable salts include halides, such as chlorides, nitrates, and, preferably, sulphates.

6

The slurry also contains silica having a BET surface area greater than 500 m²/g. Preferably the silica has a BET surface area greater than 600 m²/g. Usually the surface area is less than 1200 m²/g.

10 The silica also has a pore volume as measured by nitrogen manometry of less than 2.1 cm³/g. Preferably, the pore volume is less than 1.2 cm³/g.

Preferably, the silica is silica gel or a precipitated silica.

15 The silica preferably has a volume average particle size in the range 0.5 to 30 µm, as measured by Malvern Mastersizer[®]. More preferably, the volume average particle size of the silica is in the range 2 to 15 µm.

20 The silica is preferably present in the slurry in an amount in the range 0.2 to 40 per cent by weight with respect to the dry weight of crystalline aluminosilicate. More preferably, the amount of silica present is in the range 0.5 to 15 per cent by weight with respect to dry weight of crystalline aluminosilicate and frequently, the amount of silica used is in the range 1.0 to 5.0 by weight with respect to dry weight of crystalline aluminosilicate.

25 The crystalline aluminosilicate used in the invention can be prepared by a conventional process. For example, a zeolite of type A can be prepared by mixing together sodium aluminate and sodium silicate at a temperature within the range of ambient temperature up to boiling point to form a gel, ageing the gel with stirring at a temperature usually in the range 70 to 95° C, separating the crystalline sodium aluminosilicate thus formed, 30 washing, generally at a pH in the range 10 to 12.5, and drying. Zeolite of type P can be prepared by a similar process but zeolite type P formation is induced by the addition of type P seeds to the mixture of sodium aluminate and sodium silicate.

35 The slurry of the invention can be prepared in a number of ways. The crystalline aluminosilicate, salt of a second metal and water can be mixed in any order. A preferred method, however, comprises forming a solution of salt of a second metal at an appropriate concentration, adding the crystalline aluminosilicate with stirring and subsequently adding the silica, while the stirring is continued.

60008

5

The following tests have been used in this invention.

BET Surface Area and Pore Volume

Surface area of the silicas were measured using standard nitrogen adsorption methods of 5 Brunauer, Emmett and Teller (BET) using a multi-point method with an ASAP 2400 apparatus supplied by Micromeritics of USA. The method is consistent with the paper by S. Brunauer, P.H. Emmett and E. Teller, J. Am. Chem. Soc., 60, 309 (1938). The pore volume was determined by a single point method as described in the operation manual for the ASAP 2400 apparatus. Samples are outgassed under vacuum at 270° C for 1 hour before 10 measurement at about -196° C.

Volume average particle size

The volume average particle size of the silica is determined using a Malvern Mastersizer® model S, with a 300 RF lens and MS17 sample presentation unit. This instrument, made 15 by Malvern Instruments, Malvern, Worcestershire uses the principle of Fraunhofer diffraction, utilising a low power He/Ne laser. Before measurement the sample is dispersed ultrasonically at 25 W ultrasound power in demineralised water for 5 minutes to form an aqueous suspension. The Malvern Mastersizer® measures the volume particle size distribution of the silica. The volume average particle size (d_{50}) or 50 percentile is 20 easily obtained from the data generated by the instrument. Other percentiles, such as the 90 percentile (d_{90}), are readily obtained.

The invention is illustrated by the following non-limiting examples.

25 **EXAMPLES**

Example 1

Three slurries were prepared with the compositions given in Table 1 below.

30

35

60006

6

TABLE 1

Sample	A	B	C
Demineralised Water	57.8	57.8	57.8
Al ₂ (SO ₄) ₃ ·14 H ₂ O	1.7	1.7	1.7
Zeolite A24 (water content 7.03% by drying at 105° C)	40.5	39.5	0
Zeolite A28 (water content 13.35% by drying at 105° C)	0	0	39.5
Silica	0	1.0	1.0

The amounts given above are parts by weight.

5 Zeolite A24 is a P type zeolite sold by INEOS Silicas Limited under the trade mark Doucl A24. It had a volume average particle size as measured by Malvern Mastersizer® of 1.5 µm.

Zeolite A28 is a P type zeolite sold by INEOS Silicas Limited under the trade mark Doucl A28. It had a volume average particle size as measured by Malvern Mastersizer® of 2.8 µm.

10 The silica was a silica gel sold by INEOS Silicas Limited under the Trade Name Sorbosil AC30. It had a volume average particle size of 7.0 µm, a pore volume to nitrogen of 0.39 cm³g⁻¹ and BET surface area of 725 m²g⁻¹.

15 Three small portions were taken from each of the slurries immediately after preparation and the rheological properties of the remaining slurries were determined using a Mettler Toledo RM 180 Rheomat rheometer, at 22 ± 1° C, with a Mooney cup and bob geometry. The samples were shaken by hand prior to measurement but were not sheared vigorously. The rheometer programme consisted of shearing the sample at a set shear rate for 30 seconds, after which a shear stress measurement was taken at that shear rate. Measurements were taken at 10, 20, 30, 40, 60, 100, 200, 350 and 500 s⁻¹. The rheological properties of the small portions were similarly measured at 4 days, 24 days and 60 days after the slurries were prepared.

25 Sample A, initially and after storage, had a much higher viscosity than the other samples at all the measured shear rates. Importantly, the viscosity at low shear for Samples B and C was much lower than for Sample A. This is illustrated by the results for viscosity at a shear rate of 20 s⁻¹ shown in Table 2 below.

60006

TABLE 2

Sample		A	B	C
Viscosity at 20 s ⁻¹ (Pa s)	Initially	0.55	0.06	0.02
	After 4 days	0.58	0.06	0.10
	After 24 days	0.62	0.15	0.07
	After 60 days	0.69	0.26	0.12

5 All stock slurries showed a very slight sedimentation within 1 day, but this did not change
on storage over 2 months.

10 Material similar to Sample A was stored in a large tank and it was found that it was difficult to satisfactorily discharge the bulk of the material from the tank. In contrast, material similar to Sample B was readily discharged from a tank after storage, leaving only a minimal heel.

Example 2

Slurries were prepared with the compositions given in Table 3 below.

15

TABLE 3

Sample	D	E	F
Demineralised Water	58.0	57.6	57.6
Al ₂ (SO ₄) ₃ .14 H ₂ O	1.5	1.5	1.5
Zeolite A24 (water content 7.03% by heating at 105° C)	40.5	40.2	40.2
Silica - Sorbosil AC30	-	0.7	-
Silica - Gasil TM GM2	-	-	0.7

The amounts given above are part by weight.

The zeolite and silica (Sorbosil AC30) were as used in Example 1. GasilTM GM2 was a silica gel sold by INEOS Silicas Limited having a volume average particle size of 7.3 µm, a pore volume to nitrogen of 0.37 cm³g⁻¹ and a BET surface area of 691 m²g⁻¹.

20 The rheology profiles were measured as described in Example 1 on the samples 24 hours after preparation. The profiles of E and F were essentially similar to the profiles of

60006

8

Samples B and C, with Sample D being similar to Sample A. The viscosities at 20 s⁻¹ were as follows:

	Sample D	0.54 Pa s
	Sample E	0.01 Pa s
5	Sample F	0.01 Pa s.

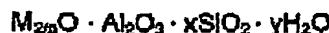
60006

9

CLAIMS

1. An aqueous slurry comprising

(a) a crystalline aluminosilicate represented by the empirical formula



wherein M represents a first metal moiety, said first metal having a valency of n, x indicates the ratio of atoms of silicon to atoms of aluminium and y indicates the ratio of molecules of water to atoms of aluminium,

(b) a salt of a second metal selected from the group consisting of Group III metals, metallic elements of Group IV, magnesium, titanium, chromium, iron, nickel, copper, zinc, zirconium and silver, said salt of a second metal being present in an amount which is sufficient to replace from about 2.0 to about 40 per cent by weight of the first metal moiety, and

(c) particulate silica having a BET surface area greater than 500 m²/g and a pore volume, as measured by nitrogen manometry of less than 2.1 cm³/g.

2. An aqueous slurry according to claim 1 characterised in that M is sodium.

3. An aqueous slurry according to claim 1 or 2 characterised in that the crystalline aluminosilicate is a zeolite P, zeolite A or zeolite X,

4. An aqueous slurry according to any one of the preceding claims characterised in that the second metal is aluminium, zirconium or tin.

5. An aqueous slurry according to any one of the preceding claims characterised in that it has a pH in the range 6 to 9.

6. An aqueous slurry according to any one of the preceding claims characterised in that the crystalline aluminosilicate has a volume average particle size in the range 0.1 to 20 µm.

7. An aqueous slurry according to any one of the preceding claims characterised in that the amount of crystalline aluminosilicate present in the slurry is in the range 20 to 50 per cent by weight calculated as dry aluminosilicate.

8. An aqueous slurry according to any one of the preceding claims characterised in that the silica has a BET surface area greater than 600 m²/g.

60006

10

9. An aqueous slurry according to any one of the preceding claims characterised in that the silica has a pore volume of less than 1.2 cm³/g.

10. An aqueous slurry according to any one of the preceding claims characterised in that the silica has a volume average particle size in the range 0.6 to 30 µm.

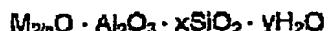
11. An aqueous slurry according to any one of the preceding claims characterised in that the amount of silica present in the slurry is in the range 0.2 to 40 per cent by weight with respect to dry weight of crystalline aluminosilicate present.

60006

11

ABSTRACT

An aqueous slurry according to the invention comprises (a) a crystalline aluminosilicate represented by the empirical formula



5 wherein M represents a first metal moiety, said first metal having a valency of n; x indicates the ratio of atoms of silicon to atoms of aluminium and y indicates the ratio of molecules of water to atoms of aluminium, (b) a salt of a second metal selected from the group consisting of Group III metals, metallic elements of Group IV, magnesium, titanium, chromium, iron, nickel, copper, zinc, zirconium and silver, said salt of a second metal
10 being present in an amount which is sufficient to replace from about 2.0 to about 40 per cent by weight of the first metal moiety, and (c) particulate silica having a BET surface area greater than 600 m²/g and a pore volume, as measured by nitrogen manometry of less than 2.1 cm³/g. The slurry is stable on storage but has a low viscosity at low shear rate.